UTILIZATION OF MICROWAVE SPECTROSCOPY TO IDENTIFY AND PROBE REACTION DYNAMICS OF HSNO, A CRUCIAL BIOLOGICAL SIGNALING MOLECULE

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Thionitrous acid (HSNO), a potential key intermediate in biological signaling pathways, has been proposed to link NO and H_2S biochemistries. Its existence and stability in vivo, however, remain controversial. By means of Fourier-transform microwave spectroscopy, we establish that HSNO is spontaneously formed in high concentration when NO and H_2S gases are simply mixed at room temperature in the presence of metallic surfaces. Our measurements reveal that HSNO is formed with high efficiency by the reaction H_2S and N_2O_3 to produce HSNO and HNO_2, where N_2O_3 is a product of NO disproportionation. These studies also suggest that further reaction of HSNO with H_2S may form HNO and HSSH. The length of the S–N bond has been derived to high precision from isotopic studies, and is found to be unusually long, 1.84 Å – the longest S–N bond reported to date for an SNO compound. The present structural and reactivity investigations of this elusive molecule provide a firm fundation to better understand its physiological chemistry and propensity to undergo S–N bond homolysis in vivo.